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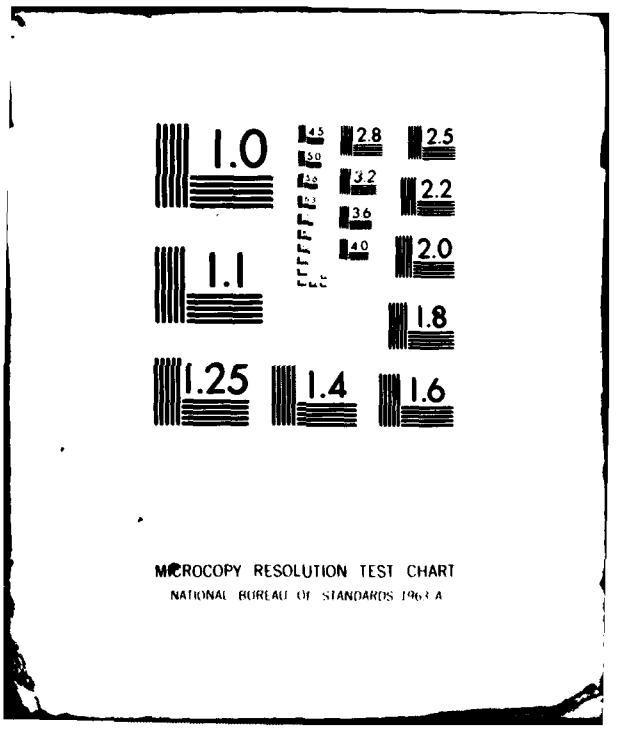
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LEVEL II

Final Technical Report

"Time-of-Flight Spectroscopy of Molecular Structure, Collision Processes, and Gas-Surface Interactions"

Principal Investigators

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AFOSR Grant 75-2864

Summary of research June 1975 - June 1980

Research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, United States Air Force.

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Tucson, Arizona 85721

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ABSTRACT

Progress in molecular physics research using time-of-flight techniques to measure velocity distributions of fragments from dissociating molecules is reported. Electron bombardment at energies between 20 and 100 eV was used to dissociate the molecules, and only fragments with kinetic energies greater than about 1 eV were detected. Both metastable hydrogen atoms and one-, two-, and three-atom hydrogenic charged fragments were detected. Special selective detectors were designed and built for metastable hydrogen atoms as well as a mass filter for identifying the mass of ionic fragments. A large portion of this work was done using the hydrogen molecule and its deuterated forms; however, heavier molecules such as methane, ethane, methanol, and ethanol, were also studied.

CONTENTS

I. Introduction

This report contains a summary of research in molecular physics conducted under AFOSR Grant 75-2864 during the period 15 June 1975 to 14 June 1980. The research was done in the Department of Physics at the University of Arizona by faculty and staff of the Department of Physics and the Optical Sciences Center.

During this period we have developed and put to use apparatus, utilizing time-of-flight techniques, to measure the velocity distribution of metastable and ionic fragments from dissociating molecules. Molecules are bombarded with a pulsed electron beam which results in some of the molecules dissociating into two or more fragments. The time for these fragments to traverse a fixed flight path is then measured, from which a velocity distribution of the fragments is obtained. An important part of this research was the development of suitable detectors to identify selected types of fragments. We have constructed a selective detector of metastable hydrogen atoms as well as a mass-filter and detector system for identification of ionic fragment masses. Much of our effort has centered on the hydrogen molecule and its isotopic variations (H_2, D_2, and HD); however, we have also obtained results on polyatomic molecules such as methane, ethane, methanol, and ethanol.

In addition to molecular fragment velocity distribution measurements, we have used the time-of-flight technique and our hydorgen atom metastable detector to measure the amount of collisional quenching of metastable hydrogen atoms when passing through several varieties of atomic and molecular species.

In the case of the hydrogen molecule, our velocity distribution measurements of metastable (2S state) atomic fragments and H^+ fragments have provided

information concerning the molecular states excited in the electron bombardment process. Although this is the simplest molecule in nature, a complete understanding of the states involved in electron bombardment excitation is not yet available. In addition to information on the repulsive (unbound) states of H_2 which result in dissociation, we were able to obtain information on some bound excited states which predissociate by transition to a repulsive state. These discrete bound vibrational levels appear as resolved structure in the fragment time-of-flight distribution.

In the case of polyatomic molecules, specific repulsive state identification is much more difficult and more general results were obtained. An example of this type of information is our study of the origin of H^+, H_2^+, and H_3^+ fragments from methanol. This work involved the ion mass filter and the use of the deuterated methanols CH_3OD, CD_3OH, and CD_3OD.

In the following sections we present a bibliography and abstracts of the seven articles published in the literature during this report period as well as a list of personnel involved with the reported research.

II. Summary of Research Publications

We give below a list of publications with their abstracts covering work done during the period 15 June 1975 and 14 June 1980.

1. "Metastable hydrogen atom detector suitable for time-of-flight studies," S. Czuchlewski, S. R. Ryan, and W. H. Wing, Reviews of Scientific Instruments 47, 1026 (1976).

ABSTRACT

A selective detection scheme for atoms in the metastable 2s state of hydrogen that provides the high spatial resolution (0.1 cm) necessary for time-of-flight atomic-beam studies is described. The scheme utilizes the Lyman α photon emitted when the metastable is de-excited in an electric field via the Stark effect. Details of construction and operation are discussed.

2. "Collisional quenching of metastable hydrogen atoms by atoms and molecules," S. R. Ryan, S. J. Czuchlewski, and M. V. McCusker, Physical Review A 16, 1892 (1977).

ABSTRACT

The deexcitation or quenching of the metastable 2S state of atomic hydrogen in collision with atoms and molecules has been studied using a beam-attenuation method in conjunction with a time-of-flight technique at velocities between 0.4×10^6 and 4×10^6 cm/sec (0.07 and 8 eV). In this regime, transfer of the metastable to the 2P state of hydrogen, followed by radiative decay to the ground state, is the dominant destruction mechanism. Absolute cross sections are reported for the quenching of H(2S) atoms in collision with the noble gases (helium-xenon), with molecules that have permanent electric-quadrupole moments (hydrogen and nitrogen), and with molecules that have permanent electric-dipole moments (ammonia, methanol, and acetone). For molecules with dipole moments, the cross sections are on the order of 10^{-13} cm^2 and vary approximately as v^{-1}. For the noble gases and the quadrupole-moment molecules, the cross sections are on the order of 10^{-14} cm^2 and vary approximately as v^{-n} where $0.3<n<0.7$. Measurements of the relative cross section for the production of ultraviolet radiation in collision with nitrogen and argon are reported, and the cross sections for the quenching of H(2S) and D(2S) in argon are compared. Data for the noble gases indicate that large-angle elastic scattering is probably not responsible for the discrepancy between theory and experiment. The data for molecular hydrogen suggest that short-range forces are important in collisions with molecules possessing a quadrupole moment.

3. "Time-of-flight study of H(2S) and D(2S) produced by electron impact on H_2, D_2, and HD: Evidence for predissociation," S. R. Ryan, J. J. Spezeski, O. F. Kalman, W. E. Lamb, Jr., L. C. McIntyre, Jr., and W. H. Wing, Physical Review A 19, 2192 (1979).

ABSTRACT

Time-of-flight spectra of H(2S) and D(2S) fragments from electron-bombardment-dissociated H_2, D_2, and HD have been observed. Structure in the kinetic-energy distributions below 1.3 eV is interpreted as arising from predissociation of bound vibrational levels. For H_2 and D_2 the primary predissociation process appears to be predissociation of the D state via the B' state. Predissociation structure for HD, although more prominent than for H_2 and D_2, is not as easily interpreted. Evidence for the direct dissociation of the B' state has also been obtained and the relative probabilities of direct dissociation and predissociation have been estimated.

4. "Mass filter and focusing ion detector for use with time-of-flight velocity distribution measurements," M. D. Burrows, S. R. Ryan, W. E. Lamb, Jr., and L. C. McIntyre, Jr., Review of Scientific Instruments 50, 1278 (1979).

ABSTRACT

A novel mass filter and focusing ion detector for time-of-flight studies of dissociative ionization fragments is described. The filter-detector combination is particularly suited for measuring the kinetic energy released in the molecular dissociation process. The mass filter utilizes a computer-controlled, time-dependent retarding potential synchronized with, and located a distance L from, a pulsed electron-bombardment ion source. Ions arriving at the filter at time t have a kinetic energy of $mL^2/2t^2$. The retarding potential varies with time as $mL^2/2et^2$, thus deflecting ions with masses less than m. Operation of the filter in a mode which provides unity mass resolution at 16 amu has been demonstrated. The detector consists of a channel electron multiplier and a focusing electrode configuration approximating that of a charged sphere above a grounded conducting plane. The planar input aperture of the detector is located just behind the mass filter along the ion flight path. The detector features high efficiency, large input aperture, low background, and simple operation. Ion transit times through the detector are small and essentially independent of the initial ion kinetic energy.

5. "Studies of H^+, H_2^+, and H_3^+ dissociative ionization fragments from methane, ethane, methanol, ethanol, and some deuterated methanols using electron-impact excitation and a time-of-flight method incorporating mass analysis," M. D. Burrows, S. R. Ryan, W. E. Lamb, Jr., and L. C. McIntyre, Jr., Journal of Chemical Physics 71, 4931 (1979).

ABSTRACT

Kinetic energy distributions and relative intensities of energetic (>1 eV) H^+, H_2^+, and H_3^+ dissociative-ionization fragments from methane, ethane, ethanol, and methanol have been measured using pulsed electron-impact excitation and a time-of-flight method incorporating a new mass analysis technique. The various deuterated analogs of H^+, H_2^+, and H_3^+ fragments were also observed from CH_3OD, CD_3OH, and CD_3OD. Results for these deuterated fragments show that energetic H_2^+ and H_3^+ fragments originate primarily from the $-CH_3$ group, rather than from H atom extraction from both the $-CH_3$ and

-OH groups. Comparisons among the kinetic energy distributions of these light fragments from CH_3OH, CD_3OD, and CD_3OH reveal no major isotope effects for fragment energies exceeding 2 eV.

6. "Dissociative ionization of H_2, D_2, and HD using electron-impact excitation," M. D. Burrows, L. C. McIntyre, Jr., S. R. Ryan, and W. E. Lamb, Jr., Physical Review A 21, 1841 (1980).

ABSTRACT

Kinetic-energy distributions of ion fragments from electron-impact bombardment of H_2, D_2, and HD have been measured at electron energies between 30 and 100 eV. In the case of H_2 these distributions at 90° are interpreted as resulting from excitation of two autoionizing states of H_2 ($^1\Sigma_g^+$ and $^1\Pi_u$) and one repulsive state of H_2^+ ($^2\Pi_u$). The shapes of the kinetic-energy distributions for H^+ from H_2 and D^+ from D_2 are substantially different, and a strong preference for H^+ over D^+ fragments from HD was observed.

7. "Time-of-flight study of H(2S) and D(2S) produced by electron impact on H_2 and D_2: Fast peaks," J. J. Spezeski, O. F. Kalman, and L. C. McIntyre, Jr., accepted for publication by Physical Review A.

ABSTRACT

Time-of-flight spectra of H(2S) and D(2S) fragments from electron-bombardment-dissociated H_2 and D_2 have been observed. Kinetic energy distributions of "fast" metastable fragments were obtained for electron bombardment energies ranging from near the threshold for fast metastable production (less than 27 eV) to 100 eV. At low bombarding energies previously unreported structure is observed in the fast peaks for both isotopes. Also, fast metastables are observed below a previously reported threshold bombarding energy. At high bombarding energies also there is evidence of unresolved structure in the fast peaks. The present data is compared with the results of earlier investigations. At low bombarding energies there are significant discrepancies between the present results and previous measurements. At high bombarding energies there is significant disagreement with a calculation that assumes a single dissociating state. The observed shift of the fast peak as a function of the bombarding electron energy is compared to predictions incorporating a form of the Wannier law. This comparison tends to confirm the presence of more than one dissociation channel yielding fast meatstables. Several excited states of H_2 and H_2^+ are discussed as possible dissociation channels contributing to the observed kinetic energy distributions.

In addition to the above articles, the following abstracts were published in the Bulletin of the American Physical Society:

1. Metastable Hydrogen Atoms Produced by Dissociative Excitation of Hydrogen-Bearing Molecules. M. McCusker, S. R. Ryan, and W. H. Wing, Bull. Am. Phys. Soc. 20, 1454 (1975).

ABSTRACT

A time-of-flight technique has been used to study the velocity and energy distributions of metastable hydrogen atoms produced by electron-impact dissociation of hydrogen-bearing molecules. All molecules investigated to date yield energetic metastable atoms including methanol, ammonia, hydrogen chloride, and various simple hydrocarbons. The spectra of H(2S) atoms from these molecules all exhibit a single peak in the energy distribution with an energy maximum between 1 and 5 eV. (Molecular hydrogen is an exception with two peaks at 0.2 and 5.3 eV). Metastable yield varies greatly with molecular species. A comparison of the spectra of similar molecular species will be discussed.

2. Ions and Metastable Hydrogen Atoms Ejected by Electron Impact on Solid Surfaces. M. Burrows, W. E. Lamb, Jr., and S. R. Ryan, Bull. Am. Phys. Soc. 20, 1455 (1975).

ABSTRACT

A time-of-flight technique has been used to study the velocity and energy distributions of ions and metastable hydrogen atoms which are ejected by the electron bombardment of solid surfaces. Energetic H(2S) atoms have been produced by electron impact on a tungsten surface covered with adsorbed hydrogen. The energy distribution of the H(2S) atoms exhibits a single energy peak near 3.5 eV. Positive ions are also ejected by electron impact from hydrogen covered tungsten surfaces. The ion velocity spectrum exhibits several distinct peaks with time-dependent amplitudes. The mass corresponding to each velocity peak can be determined by a simultaneous measurement of the energy and velocity of the ejected ions. The fastest and most abundant species is H^+ with a maximum at an energy of 13 eV. The H^+ ion appears several minutes after the onset of electron bombardment. Several slower ion peaks with energy between 4 and 12 eV and masses between 16 and 18 amu have been seen. These ion species are present immediately after surface preparation and are exhausted by extended bombardment.

III. Personnel

The following is a list of scientific personnel involved with this research:

W. E. Lamb, Jr., Professor of Physics and Optical Sciences, University of Arizona
Principal Investigator 1975-1980

S. R. Ryan, presently Assistant Professor of Physics, University of Oklahoma
Principal Investigator 1975-1977

L. C. McIntyre, Jr., Professor of Physics, University of Arizona
Principal Investigator 1977-1980

W. H. Wing, Professor of Physics and Optical Sciences, University of Arizona
Faculty Associate 1975-1977

J. J. Spezeski
Research Associate 1978-1980

O. F. Kalman
Research Associate 1978-1980

Bruce DaCosta
Research Assistant 1977

Mike Burrows
Research Assistant 1975-1979

Charles Drutman
Research Assistant 1977-1978

Bruce Kittams
Research Assistant 1979-1980

In addition, S. J. Czuchlewski and M. V. McCusker were associated with this project prior to 1974 when it was moved from Yale to the University of Arizona.

Mike Burrows received his Ph.D. (Chemistry) from the University of Arizona in June 1979. His dissertation was entitled "An ion time-of-flight spectrometer with mass analysis."

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Progress in molecular physics research using time-of-flight techniques to measure velocity distributions of fragments from dissociating molecules is reported. Electron bombardment at energies between 20 and 100 eV was used to dissociate the molecules, and only fragments with kinetic energies greater than about 1 eV were detected. Both metastable hydrogen atoms and one-, two-, and three-atom hydrogenic charged fragments were detected. Special selective detectors were designed and built for metastable hydrogen atoms as well as a

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